Methylmercury Control Study Progress Report

California Department of Corrections and Rehabilitation

Deuel Vocational Institution

October 2015

GHD Inc.
3831 North Freeway Blvd Suite 220 Sacramento CA 95834 USA
T 1 916 372 6606 F 1 916 372 6616 E sacramento@ghd.com W www.ghd.com

Contents

Appendices

1. Introduction

In 2012, California Department of Corrections and Rehabilitation (CDCR) submitted a Control Study Workplan (Workplan) to the Central Valley Region Water Quality Control Board (Regional Board). The Control Study Work Plan initiated the effort needed to bring Deuel Vocational Institute (DVI) into compliance with Phase 1 of the Delta Mercury Control Program (DMCP). The purpose of Phase 1 is to develop control studies which identify methods in controlling methylmercury sources to achieve DVI's methylmercury waste load allocation of 0.021 g/yr.

Phase 1 of the DMCP has been implemented by the Regional Board using an "Adaptive Management Approach" whereby Workplans have been developed by municipal wastewater dischargers to the Delta with support from a Technical Advisory Committee (TAC) as well as Regional Board Staff. The TAC assists dischargers by making recommendations in developing and implementing the control studies of the Phase 1 Work Plan. By October 20th, 2015 the Regional Board requires that dischargers responsible for Control Studies submit reports documenting their progress toward meeting the objectives of the Control Study Workplan. After the Progress Report is reviewed by the TAC and Staff it will be submitted to the Regional Board.

The Control Study Work Plan prepared by GHD on behalf of CDCR developed two study objectives to meet DVI's methylmercury waste load allocation. This progress report summarizes the results of these study objectives.

2. Control Study Progress

Study Objective 1

Study Objective 1 was developed to determine whether inorganic and methylated mercury concentration is reduced by; not reduced by; or generated by the advanced wastewater treatment plant (WWTP) processes. By testing samples of WWTP influent and effluent for mercury and methylated mercury at the proposed sampling points the Control Measures of Study Objective 1 were addressed. From February to July, of 2013, WWTP influent and effluent samples were collected for each month. The samples were collected according to the USEPA Method 1669 and analyzed using the USEPA method 1630 for methylmercury and 1631E for total mercury consistent with the quality assurance procedures specified in the Control Study Workplan. A description of sampling collection methods and discussion of Quality Assurance/Quality Control results is included in Appendix A. Laboratory test results for both methylmercury and total mercury are included in Appendices B and C. The resulting concentrations measured within the aforementioned samples are shown in Table 1.0 below and will be referenced throughout the report.

Table 1.0

Sampling Month 2013	Methylmercury Conc. (ng/L)[1]		Total Mercury Conc. (ng/L)[2]	
	Influent	Effluent	Influent	Effluent
February	0.67	0.02	10.3	ND
March	0.54	0.03	17.6	1.02
April	0.45	0.04	248	1.12
May	0.44	0.04	67.2	ND
June	0.48	0.06	28.4	0.590
July	0.92	0.02	51.6	0.82

1) Method Detection limit of 0.02 ng/L
2) Method Detection limit of 0.4 ng/L

DVI's Workplan proposed several control measures to test the mechanisms underlying the study and study objectives hypothesis. Below, each proposed control measure identified in DVI's Workplan is discussed in relation to the sampling test results.

a. **Total mercury and methylmercury concentrations present in the WWTP influent.**

The sampling results indicate a presence of both total mercury and methylmercury concentrations within the WWTP influent. The influent concentrations of total mercury vary from 10 to 248 ng/L while the influent concentrations of methylmercury range from 0.45 to 0.92 ng/L. It's interesting to note that concentrations of total mercury in the influent vary widely as indicated with the largest concentration nearly 25 times that of the smallest concentration. However, influent concentrations of methylmercury have a much narrower range with the largest concentration about twice that of the smallest. It's hypothesized that increasing wastewater flows over the study period as noted later in Section 2.f may have had the effect of providing enough scour to wash down mercury laden sediment to the wastewater treatment plant to create a onetime spike in mercury concentrations. As explained in the Workplan, DVI had installed water saving fixtures in the prison that have acted to reduce flows in the collection system resulting in increased sediment in the system. The greater flows noted in Section 2.f may have mobilized the sediment washing it down to the treatment plant resulting in greater concentrations.

The relatively narrow range of methylmercury isn't a surprise since it is not anticipated that increased wastewater flows would have a significant impact on methylmercury concentrations in the influent. On the contrary, it is expected that sustained increased flows may actually help to reduce the formation of methylmercury in the collection system. As theorized in the Workplan, sedimentation in the collection system may present a possible store of mercury and methylmercury as well as conditions favorable to the continued methylation of inorganic mercury, specifically anaerobic conditions for bacteria and residence time with nutrient rich sediment. Reducing the amount of sediment in the collection system may in the long run, reduce the concentrations of methylmercury in the influent.

Nonetheless, the test results for the influent show that total mercury and methylmercury are indeed present in the influent.

b. Possible creation of methylmercury in DVI's collection system.

Because the influent sampling point marks the convergence of the collection system the influent sampling results do not provide any information to imply specific source(s) of methylmercury. However, as theorized in the Workplan and noted in the previous Section, sediment in the sewer collection system may present conditions favorable to the methylation of inorganic mercury, specifically anaerobic conditions for bacteria and residence time with nutrient rich sediment. With confirmation of methylmercury in the influent, it is possible that the source of the methylmercury is the methylation of inorganic mercury present in the collection system.

c. Possible creation and likely removal of methylated mercury by the treatment plant.

Comparing the Influent and Effluent methylmercury concentrations shows that the WWTP is effectively removing methylated mercury and inorganic mercury. There is no evidence to support the hypothesis that the treatment plant processes are contributing to the production of methylated mercury. Similarly, there is no evidence to support the hypothesis that the treatment plant itself is a source of inorganic mercury. Regardless, the concentrations of both mercury species are significantly reduced by the treatment plant.

d. Methylmercury and inorganic mercury removal rate by treatment process.

Ratios of effluent to influent methylmercury and inorganic mercury concentrations were calculated to determine the removal efficiencies of the WWTP. Removal efficiencies higher than 100% would indicate methylmercury or inorganic mercury generated by treatment plant processes. Efficiencies less than 100% indicate a reduction in methylmercury or inorganic mercury by treatment plant processes. According to *A Review of Methylmercury and Inorganic Mercury Discharges from NPDES Facilities in California's Central Valley* Staff Report Dated May 2010 (Bosworth, et al. 2010), 14 of 23 WWTPs had average effluent to influent methylmercury ratios less than or equal to 10%. Also, 5 of 8 WWTPs that submitted ratios of effluent inorganic mercury and influent inorganic mercury concentrations had an average effluent to influent inorganic mercury ratio less than or equal to 5%. The average effluent to influent methylmercury ratio for DVI was 6.88%; and the average effluent to influent inorganic mercury ratio was 2.4% for the 6-month sample period as shown in Table 2.0 below. Relative to the other WWTPs identified by Bosworth, et al. 2010, the DVI WWTP appears to have methylmercury and inorganic mercury removal rates that are consistent with the wastewater treatment plants in the study.

It's important to note that the test results data for removal efficiency for both methylmercury and inorganic mercury is highly variable. There appears to be an increasing trend for methylmercury such that the effluent to influent concentration rises over the six month study period with the exception of July indicating a decrease in the plants removal efficiency for methylmecury for the period from February to June. Based on a discussion with the plant supervisor there were no significant changes in plant operations or processes during this time period which may have had an impact on effluent methylmercury concentrations. Possible impacts of seasonal effects on the removal efficiency are discussed in the next Section. Test results for inorganic mercury also show a high degree of variability although there is no increasing trend such as that for the methylmercury concentrations. The results appear to be random. Also, there appears to be no correlation between methylmercury removal efficiencies and inorganic mercury removal efficiency.

An important implication of the results is that lowering methylmercury concentrations in the influent does not result in a corresponding drop in effluent concentrations. For example, influent methylmercury concentrations show a decreasing trend from February to June while effluent concentrations are increasing. One possibility is that a threshold exists for methylmercury removal such that influent concentrations below a certain value (lower than present concentrations) would result in removal efficiency which holds constant. The other possibility is that no threshold exists and the treatment plants capacity for methylmercury removal is independent of influent concentrations. Whether the former or the latter holds true, it appears that source control upstream of the facility would not have an impact on methylmercury concentrations in the effluent.

Table 2.0

Month of Sample 2013	MeHg Removal Efficiency %	Hg Removal Efficiency %
February	2.98	3.9
March	5.55	5.8
April	8.88	0.45
May	9.09	0.59
June	12.5	2.08
July	2.24	1.58
Average	6.88	2.4

e. **Possible seasonal effects on mercury species loading and discharges at the WWTP specifically, but not exclusive to, wet weather I/I events.**

Infiltration and Inflow

The Workplan hypothesizes that infiltration and inflow (I/I) into the sewer collection system from high groundwater as a result of increased precipitation during wetter months may have an impact on mercury species concentrations at the treatment plant. Specifically, the Workplan theorizes that it would be possible for wastewater in the collection system and related constituents such as inorganic mercury and methylmercury to be transported into the soil during drier months when the water table is lower then reintroduced into the collection system through I/I during wetter months when the water table is higher.

During the period which samples were collected (February to July) DVI received approximately 1.60 inches of precipitation, a relatively low amount compared to the 6-inch average for that period. Prior to this period there was no precipitation recorded in January and 3.4 inches recorded in December of 2012. Precipitation events greater than 0.10 inches are shown in Table 3.0. It's hard to quantify the impacts that the measured rainfall may have had in mercury species loading. Increased wastewater flows were recorded over the study period as noted in Section 2.f but it seems to correlate with an increase in inmate population. Although the portion of increased flows from I/I is indeterminate it remains a point of interest due to the depth at which the water table is present throughout the site. Based on ground water monitoring well reports included in Appendix G, the depth of ground water varies from approximately 4 to 9 feet per location. It is expected that a significant portion of the collection system exists within this range and is subject to I/I. The reports also show an increase in groundwater depth of 1.5 feet from March to July. Nonetheless, because of the lack in frequent precipitation events and ground water data there is not enough information to present meaningful data to validate or invalidate any correlation the effects precipitation may have on mercury species loading and discharges at the WWTP.

Table 3.0

Precipitation Events > 0.10"	Precipitation (in)
2012 December 3	0.59
2012 December 5	0.55
2012 December 17	0.25
2012 December 24	1.55
2012 December 26	0.20
2013 February 20	0.24
2013 March 30	0.18
2013 April 1	0.36
2013 April 4	0.61

<u>Seasonal Temperature Changes</u>

Influent Methylmercury: The 6-month sample period experienced a typical steady increase in temperature, from an average high of 45 to 91°F. While some municipal WWTPs have shown an increase in influent concentrations during spring or summer (Bosworth, et al. 2010) this does not seem to be the case for DVI. Influent concentrations decreased from 0.67 ng/L in February to 0.44 ng/L by May. A possibility for this decrease in concentration may be due to the increase in wastewater flows. This is discussed further in paragraph 2.f below.

Effluent Methylmercury: Higher temperatures have shown to correlate with an increase in effluent methylmercury concentrations at several WWTPs (Bosworth, et al. 2010). With the exception of July, this trend is present at DVI as well. Starting with an effluent methylmercury concentration of 0.02 ng/L in February the concentration increases to 0.06 ng/L by June.

Influent/Effluent Inorganic Mercury: The concentrations observed show no signs of a seasonal trend for Influent or Effluent. Influent concentrations varied from 10.25 to 248 ng/L; and effluent concentrations varied from the ND limit of 0.4 (or lower) to 1.115 ng/L. This is consistent with the data collected in the report by Bosworth, et al. 2010 which notes that no obvious relationship between seasonality and treatment processes seem to exist concerning inorganic mercury effluent concentrations among WWTPs; and there was not enough information to discern any seasonal patterns for influent concentrations.

f. Total mercury and methylmercury in the WWTP influent relative to DVI population.

According to the CDCR Office of Research the DVI experienced a significant increase in population each month during the 6-month sampling period. As expected, an increase in wastewater influent was also observed during this time as shown in Table 4.0.

Table 4.0

Month	Population Percent[(1)] Occupied	Avg WWTP influent (mgd)
February	134.3	0.40
March	138.1	0.42
April	143.2	0.49
May	151.5	0.50
June	157.9	0.46
July	166.0	0.50

1) CDCR Office of Research Monthly Total Population Report Archive 2013

As mentioned in Section e, it could be possible that an increase in wastewater flows could decrease influent methylmercury concentrations. This hypothesis is based on the possibility that the source within the collection system introduces methylmercury independently of wastewater production. This would suggest that the observed decrease in influent methylmercury concentrations is the result of dilution from increased wastewater flow rather than a decrease in mass loading.

As mentioned previously in Section 2.a, increasing wastewater flows over the study period may have had the effect of providing enough scour to wash down mercury laden sediment to the wastewater treatment plant to create a temporary spike in influent mercury concentrations as shown in Table 1.0. DVI had installed water saving fixtures in the prison that have acted to reduce flows in the collection system possibly resulting in increased sediment in the system. The greater flows noted in Section 2.f may have mobilized the sediment washing it down to the treatment plant resulting in greater concentrations.

Table 5.0 below shows the influent flow rate; methylmercury concentration; and the calculated mass loading rate of methylmercury on the day each sample was collected.

Table 5.0

Sample Date	Influent Flow per Sample Date (L/day)	MeHg Concentration (ng/L)	MeHg Mass Loading (mg/d)
February 2	1,563,769	0.67	1.05
March 13	1,545,807	0.54	0.83
April 2	1,569,882	0.45	0.71
May 14	2,031,513	0.44	0.89
June 12	1,815,056	0.48	0.87
July 23	1,991,819	0.92	1.83

It's hard to draw any conclusions from these discrete results from six sampling events over six months. It appears that methylmercury concentrations are fairly independent of the Influent Flow rates on those particular days when samples were taken although it seems possible that methylmercury may decrease as the wastewater flows increase as previously suggested. Obviously, to what extent concentrations decrease impacts the mass loading rate on the wastewater treatment plant. The data seem to suggest that concentrations don't decrease significantly with increased flow rates and in fact rise in some instances such that the mass loading increases with increased flow rates. Nonetheless, the data set isn't large enough to establish any clear trends or not. The test results could be influenced by wastewater diurnal flow patterns such that sampling times during the day surely impact the Influent Flow rate and which may impact the methylmercury concentrations in the influent.

Study Objective 2:

The intent of Study Objective 2 was to test the hypothesis that the concentration of inorganic mercury and methylated mercury in and throughout the collection system can be reduced by Source Control. When DVI's Workplan, was created, they were already in compliance with methylmercury waste load allocations of less than 0.021 g/yr with a discharge of 0.013 g/yr based on non-detect concentrations of 0.02 ng/L from effluent testing done over the period August 2011 to July 2012. The influent and effluent testing commenced as part of the Study provided results that methylmercury and mercury were indeed in the influent but that the treatment plant was removing them from the plants discharge. Furthermore, due to the nature by which the treatment plant removes methylmercury as discussed in Section 2.d it is evident that for any source control upstream of plant to be effective would require reducing concentrations within the collection systems to levels lower than plant effluent concentrations. This would essentially require source elimination, as typically the treatment plants methylmercury effluent is non-detect.

Since DVI was meeting their waste load allocation through the treatment plant, implementing Study Objective 2 to test the hypothesis that the concentration of inorganic mercury and methylated mercury in and throughout the collection system can be reduced by Source Control seemed an unnecessary expenditure of State and tax payer money. As such, DVI has not implemented Study Objective 2 pending review by Regional Board of its Progress Report.

3. Conclusion

With the fulfillment of Study Objective 1 complete, the continuation of best management practices of DVI's treatment plant has been identified as the primary source control for meeting the waste load allocation. It should also be noted that although the effluent methylmercury concentrations shown in Table 1.0 are above non-detect levels, concentrations were observed to be non-detect for the remainder of 2013. These non-detect levels of methylmercury are typical of 2012 (as previously mentioned) as well as 2014 demonstrating that the wastewater treatment plant is an effective method of source control in meeting the methylmercury waste load allocation. The cumulative effluent methylmercury mass loading from February 2013 to January 2014 as shown in Appendix B is less than the waste load allocation for DVI which is .021 g/year despite having greater than normal concentrations of methylmercury in their effluent over the study period. As discussed in Section 2.d, it’s not evident what caused effluent methylmercury concentrations to rise over the study period but it’s clear from more than two years of test results before and after the study period that DVI can consistently meet its waste load allocation.

Moreover, it is expected that the treatment plant will remain fully capable of handling present and future wastewater flow rates; as the institution’s population percent occupied has varied between 130 and 167% since the 6 month study period in 2013. Also CDCR currently does not plan on pursuing any developments at DVI which would increase the staff or inmate population at DVI within the foreseeable future. Given that significant operational changes and additional infrastructure are also unlikely to occur, it is expected that no additional sources of mercury species will be introduced into the collection system. Considering the recently constructed treatment plant will face little or no changes in wastewater flows, mercury loading, and methylmercury loading it is likely that the facility will act as a reliable form of source control in meeting DVIs waste load allocation.

It is recommended that, upon review of the Technical Advisory Committee, that this Progress Report concludes DVI’s phase 1 requirements.